Glycerol Valorization Over Cu and Pt Catalysts Under A Thermal Controled Photocatalytic Reaction

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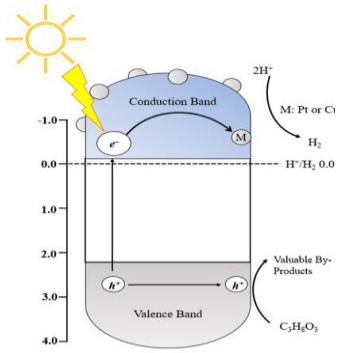

The incorporation of Pt is a commonly employed alternative to enhance catalytic efficiency, but its high cost may limit scalability in the short term. Cu emerges as a promising alternative, despite being less efficient than Pt. However, using a simple photocatalytic method with moderate temperature variation, it was possible to significantly increase the activity of Cu-based catalysts, even at a dosage of less than 1% of the metal, with approximately 100 mL of H_2 produced at 60°C. Temperature variation in the photocatalytic oxidation of glycerol had a significant impact on H_2 production, yielding results comparable to those obtained when employing Cu or Pt as catalysts. It was observed that TiO_2@Pt was particularly sensitive to temperature variation in the production process of dihydroxyacetone. These results contribute to the valorization of glycerol through renewable routes.

Introduction

The supply of glycerol has grown substantially with the advent of renewable fuel production routes, such as biodiesel. As a byproduct, it accounts for about 10% of the biodiesel produced, and despite its low toxicity to the environment, the presence of salts, metals, and its highly alkaline pH make it a waste material with high availability and insufficient demand, rendering it a low-value product with potential for conversion into high-value-added products. In recent years, glycerol has been used as a raw material for the synthesis of compounds such as lactic acid, propanol, glycolic acid, dihydroxyacetone, and H_2. The photocatalytic route has shown great potential for the valorization of glycerol, particularly its conversion to H_2. Despite this promising alternative, there are intrinsic factors to the catalysts commonly employed in these studies, such as TiO_2, which make their application less competitive, such as low activity under visible light [1,2]. Doping with other metals on the TiO_2 surface is an alternative for working at lower energy levels, such as radiation in the visible spectrum. It offers a mechanism for minimizing electron/hole pair recombination [3]. Aiming to increase the performance of hydrogen production via photocatalytic means, several studies have reported the doping of TiO_2 with noble metals, such as gold [4], silver [5], platinum [6], and palladium [7]. Alternatively, transition metals are an attractive alternative from a cost-benefit perspective. This work aims to evaluate hydrogen production via photocatalytic means using TiO_2 doped with copper and platinum in the presence of glycerol as substrate, investigating the influence of process variables such as catalyst composition, temperature and formation of value-added products.

Material and Methods

TiO_2 was adopted as the reference catalyst, being modified with Cu and Pt doping through the photodeposition method. Initially, Cu and Pt precursors were equilibrated with TiO_2 in a 10% (v/v) methanol solution for 2 hours, followed by irradiation with a 300 W Xe lamp. The percentages of Cu and Pt were fixed at 0.7 and 0.3% (wt), respectively. Reactions were conducted in a glass reactor containing 170 mL of 10% glycerol solution, with a catalyst concentration of 0.4 $g.L^{-1}$, and irradiation for 3 hours (Xe, 300 W). Tests were carried out at 20, 40, and 60 °C. The gas phase was analyzed by gas chromatography (GC-TCD, Agilent). Liquid-phase co-products were evaluated by HPLC (Shimadzu) equipped with a Rezex ROA-Organic Acid (8%) column.

Results and Discussion

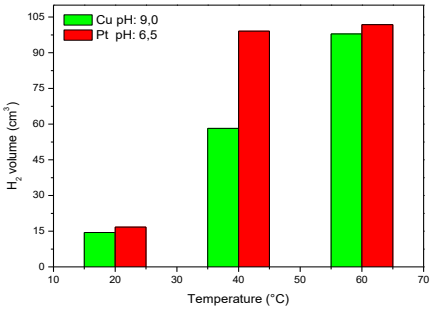

Figure 1. H_2 production over TiO_2@M (M = Pt and Cu) under different temperature and pH conditions, Glicerol concentration: 10%.

Figure 1 highlights the evolution of H_2 results on TiO_2@Pt and TiO_2@Cu catalysts. Previous studies indicated optimal pH values of 6.5 and 9.0 for TiO_2@Cu and TiO_2@Pt, respectively. The effect of

temperature on the photocatalytic performance of both materials was evaluated in the range of 20 – 60°C, under different pH values. The reaction pH, evaluated at a temperature of 40°C, was found to be significant, with TiO_2@Pt showing a prominent increase in activity at pH = 6.5. TiO_2@Cu, however, exhibited better results at pH = 9.0. The same trend was observed for the dosage of metal deposited on TiO_2@Cu, where 0.7% Cu was defined as the minimum relevant percentage for H_2 production. Higher quantities did not increase total H_2 production, also at 40°C. Conversely, Pt did not exhibit any effect on photocatalytic activity with successive increases.

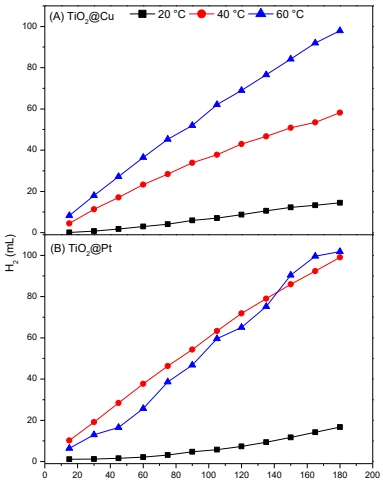

Figure 2. Kinectic H_2 evolution over TiO_2@M (M = (A) Cu, (B) Pt) under different temperatures. Glicerol concentration: 10%, pH: 9,0 and pH: 6,5.

When evaluating the effect of temperature on the catalysts, a similar trend is observed at 20 and 40°C, with Pt doping resulting in a higher volume of H_2 produced. The results indicate that in this temperature range, the reduction effect on the recombination rate of electron-hole pairs was more pronounced in the presence of Pt as a dopant. This observation is well-supported in the literature, which reports Pt as an excellent co-catalyst applied to the photocatalytic process of H_2 production. At 60°C, the photocatalytic performance for both catalysts is similar, as corroborated by the kinetic profiles presented in Figure 2. The observed result is supported when evaluating the lower resistance of Cu.

The results obtained for glycerol oxidation products on TiO_2@Cu showed low temperature influence on the production of dihydroxyacetone (DHA), with concentrations ranging from 102 to 170 $mg.L^{-1}$ after 3 hours of reaction for the tested temperature range. Meanwhile, TiO_2@Pt exhibited greater susceptibility to temperature changes in DHA production, with concentrations of 195, 235, and 300 $mg.L_{-1}$ at 20, 40, and 60°C, respectively. For both catalysts, the volume of CO_2 did not show a significant increase in the temperature range employed, remaining between 0.72 and 1.10 mL.

Conclusions

The use of temperature variation in the photocatalytic oxidation reaction of glycerol demonstrated a highly significant effect on H_2 evolution, allowing for similar results to be achieved when comparing the use of Cu or Pt as dopants. TiO_2@Pt proved to be more susceptible to temperature variation for dihydroxyacetone production. Overall, the results support the exploration of photocatalysis and the use of renewable routes for biomass valorization using low-cost catalysts.

Acknowledgments

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